

AMENDMENTS TO THE CLAIMS

A detailed listing of all claims that are, or were, in the present application, irrespective of whether the claim(s) remains under examination in the application are presented below. The claims are presented in ascending order and each includes one status identifier.

1. (Withdrawn) A method of producing an alumina-supported catalyst, which comprises the following steps:

a first impregnation step in which an initial alumina support material is impregnated with a source of a 2-valent metal capable of forming a spinel compound with alumina;

a first calcination step in which the impregnated alumina support material is calcined at a temperature of at least 550°C to produce a modified alumina support material;

a second impregnation step in which the modified alumina support material is impregnated with a source of catalytically active metal; and

a second calcination step in which the impregnated modified support material is calcined at a temperature of at least 150°C.

2. (Withdrawn) A method as claimed in Claim 1, in which the initial alumina support material at least predominantly comprises γ -alumina.

3. (Withdrawn) A method as claimed in Claim 1, in which the impregnated modified support material is calcined at a temperature of up to 600°C.

4. (Withdrawn) A method as claimed in Claim 1, in which the impregnated and calcined modified support has a pore volume measured by nitrogen BET in which at least half the pore volume is constituted by pores larger than 30 nm in diameter.

5. (Withdrawn) A method as claimed in Claim 1, in which the initial alumina support material has a specific surface area in the range 100 to 300 m²/g.
6. (Withdrawn) A method as claimed in Claim 1, in which the initial alumina support material comprises essentially spherical particles having a particle size range whereby at least 80 volume % fall in the range 25 to 150 µm.
7. (Withdrawn) A method as claimed in Claim 1, in which the initial alumina support material has a pore volume greater than 0.2cm³/g, preferably greater than 0.4cm³/g.
8. (Withdrawn) A method as claimed in Claim 1, in which the first calcination step is carried out at a temperature in the range 800 to 1200°C.
9. (Withdrawn) A method as claimed in Claim 1, in which the first calcination step is carried out at a temperature in the range 900 to 1200°C.
10. (Withdrawn) A method as claimed in Claim 1, in which the modified alumina support has a surface area of less than 40 m²/g.
11. (Withdrawn) A method as claimed in Claim 1, in which the modified alumina support has an ASTM attrition value of less than 20 % by weight of fines produced by 5 hours testing.

12. (Withdrawn) A method as claimed in Claim 1, in which the modified alumina support has an ASTM attrition value of less than 8 % by weight of fines produced by 5 hours testing.
13. (Withdrawn) A method as claimed in Claim 1, in which the modified alumina support comprises at least 10 % by weight of alfa-alumina.
14. (Withdrawn Amended) A method as claimed in Claim 1, in which the source of a 2-valent metal comprises a source of cobalt, zinc, magnesium, manganese, nickel or iron.
15. (Withdrawn) A method as claimed in Claim 1, in which the source of a 2-valent metal does not comprise a source of cobalt.
16. (Withdrawn) A method as claimed in Claim 1, in which the source of a 2-valent metal comprises nickel.
17. (Withdrawn) A method as claimed in Claim 1, in which the source of a 2-valent metal comprises nickel in an amount of less than 20 wt% of the final reduced catalyst.
18. (Withdrawn) A method as claimed in Claim 1, in which the source of a 2-valent metal comprises nickel in an amount of less than 8 wt% of the final reduced catalyst.

19. (Withdrawn) A method as claimed in Claim 1, which includes additionally impregnating or co-impregnating the alumina support material with a promoter.
20. (Withdrawn) A method as claimed in Claim 19, in which the promoter comprises platinum or rhenium.
21. (Withdrawn) A method as claimed in Claim 20, in which the promoter is rhenium and the source of rhenium is selected from perrhenic acid (HReO_4), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).
22. (Withdrawn) A method as claimed in Claim 1, which includes additionally incorporating a stabiliser into the alumina support material with a stabiliser.
23. (Withdrawn) A method as claimed in Claim 22, in which the stabiliser comprises lanthanum.
24. (Withdrawn) A method as claimed in Claim 1, in which the first impregnation step comprises an incipient wetness treatment in which an aqueous solution of the 2-valent metal compound is mixed with the dry support material until the pores are filled, and the impregnated support is then dried, prior to the first calcining step.

25. (Withdrawn) A method as claimed in Claim 1, in which the source of catalytically active metal comprises a source of cobalt.

26. (Withdrawn) A method as claimed in Claim 25, in which the source of cobalt is selected from cobalt nitrate ($\text{Co}(\text{NO}_3)_2$), cobalt acetate(s), cobalt halide(s), cobalt carbonyl(s), cobalt oxalate(s), cobalt phosphate(s), cobalt carbonate(s), cobalt (hexa)amine salt(s) and organic cobalt compounds.

27. (Withdrawn) A method as claimed in Claim 1, in which the second impregnation step comprises an incipient wetness treatment in which an aqueous solution of a cobalt compound and optionally a rhenium compound is mixed with the modified support material until the pores are filled and the impregnated modified support material is then dried, prior to the second calcination step.

28. (Withdrawn) A method as claimed in Claim Claim 27, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger than the measured pore volume of the catalyst support.

29. (Withdrawn) A method as claimed in Claim 27, in which drying is carried out at 80 to 120°C.

30. (Withdrawn) A method as claimed in Claim 1, in which, after the second calcination step, the alumina-supported catalyst material is activated.
31. (Withdrawn) A method as claimed in Claim 30, in which the activation step comprises reduction of a substantial portion of the catalytically active metal compound present to the metal.
32. (Withdrawn) A method as claimed in Claim 31, in which the reduction is carried out by treating the catalyst material with a reducing gas.
33. (Withdrawn) A method as claimed in Claim 32, in which the reducing agent is hydrogen and/or carbon monoxide, optionally mixed with an inert gas.
34. (Withdrawn) A method as claimed in any of Claims 31, in which the reduction is carried out at an activation temperature of 250 to 500°C.
35. (Withdrawn) A method as claimed in Claim 34, in which the activation temperature is in the range 300 to 450°C.
36. (Withdrawn) A method as claimed in Claim 1, in which, prior to impregnation, the alumina support has an ASTM attrition value of less than 30% by weight of fines produced by 5 hours testing.

37. (Withdrawn) A method as claimed in Claim 36 in which the ASTM value is less than 20%.

38. (Previously Presented) An alumina-supported catalyst produced by a method which comprises the following steps:

a first impregnation step in which an initial alumina support material is impregnated with a source of a 2-valent metal capable of forming a spinel compound with alumina;

a first calcination step in which the impregnated alumina support material is calcined at a temperature of at least 550°C to produce a modified alumina support material;

a second impregnation step in which the modified alumina support material is impregnated with a source of catalytically active metal;

and a second calcination step in which the impregnated modified support material is calcined at a temperature of at least 150°C.

39. (Original) A catalyst as claimed in Claim 38, in which the catalytically active metal and optionally the 2-valent metal are cobalt, and the cobalt content of the catalyst is from 10 to 40% by weight.

40. (Original) A catalyst as claimed in Claim 39, in which the cobalt content is from 15 to 25% by weight.

41. (Previously Presented) A catalyst as claimed in Claim 38, incorporating less than 3% by weight of a promoter.

42. (Original) A catalyst as claimed in Claim 41, in which the promoter is rhenium or platinum.

43. (Previously Presented) A catalyst as claimed in Claim 38, in which the initial support material predominantly comprises γ -alumina.

44. (Original) A catalyst as claimed in Claim 43, in which the γ -alumina is stabilised with a stabilising agent, optionally lanthanum.

45. (Previously Presented) A catalyst as claimed in Claim 38, in which the alumina support material includes a binder.

46. (Original) A catalyst as claimed in Claim 45, in which the binder represents less than 25% by weight of the catalyst.

47. (Previously Presented) A catalyst as claimed in Claim 45, in which the binder is an alumina-containing binder material.

48. (Previously Presented) A catalyst as claimed in Claim 38, in which the specific surface area of the prepared catalyst, comprising the cobalt on the modified support, is up to 150 m²/g.

49. (Previously Presented) A catalyst as claimed in Claim 38, in which the pore volume of the prepared catalyst is from 0.05 to 0.7 cm³/g.
50. (Previously Presented) A catalyst as claimed in Claim 38, in which the pore diameter of the prepared catalyst is at least 10 nm, preferably at least 18 nm.
51. (Withdrawn) The use of a catalyst as claimed in Claim 48 in a Fischer-Tropsch synthesis reaction.
52. (Withdrawn) A use as claimed in Claim 51, in which the reaction is carried out in a slurry bubble column reactor.
53. (Withdrawn) A use as claimed in Claim 52, in which H₂ and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H₂ and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.
54. (Withdrawn) A process for the production of hydrocarbons which comprise subjecting H₂ and CO gases to a Fischer-Tropsch synthesis reaction in a reactor in the presence of a catalyst as claimed in Claim 38.

55. (Withdrawn) A process as claimed in Claim 54, in which the reaction is a three-phase reaction in which the reactants are gaseous, the product is at least partially liquid and the catalyst is solid.

56. (Withdrawn) A process as claimed in Claim 55, in which the reaction is carried out in a slurry bubble column reactor.

57. (Withdrawn) A process as claimed in Claim 56, in which the H₂ and CO are supplied to a slurry in the reactor, the slurry comprising the catalyst in suspension in a liquid including the reaction products of the H₂ and CO, the catalyst being maintained in suspension in the slurry at least partly by the motion of the gas supplied to the slurry.

58. (Withdrawn) A process as claimed in Claim 54, in which the reaction temperature is in the range 190-250°C.

59. (Withdrawn) A process as claimed in Claim 58, in which the reaction temperature is in the range 200-230°C.

60. (Withdrawn) A process as claimed in Claim 54, in which the reaction pressure is in the range 10-60 bar.

61. (Withdrawn) A process as claimed in Claim 60, in which the reaction pressure is in the range 15 to 30 bar.
62. (Withdrawn) A process as claimed in Claim 54, in which the H_2/CO ratio of the gases supplied to the Fischer- Tropsch synthesis reactor is in the range 1.1 to 2.2.
63. (Withdrawn) A process as claimed in Claim 62, in which the H_2/CO ratio is in the range 1.5 to 1.95.
64. (Withdrawn) A process as claimed in Claim 54, in which the superficial gas velocity in the reactor is in the range 5 to 60 cm/s.
65. (Withdrawn) A process as claimed in Claim 64 in which the superficial gas velocity is in the range 20 to 40 cm/s.
66. (Withdrawn) A process as claimed in Claim 54, in which the product of the Fischer-Tropsch synthesis reaction is subsequently subjected to post-processmg.
67. (Withdrawn) A process as claimed in Claim 66 in which the post-processing is selected from de-waxing, hydro-isomerisation, hydro-cracking and combinations of these.

68. (Withdrawn) A method for the production of an alumina support for a catalyst, which comprises impregnating an initial alumina support material with a source of a 2-valent metal capable of forming a spinel compound with alumina, and calcining the impregnated alumina at a temperature of at least 550°C.
69. (Withdrawn) A method as claimed in Claim 68, in which the initial alumina support material at least predominantly comprises γ -alumina.
70. (Withdrawn) A method as claimed in Claim 68, in which the initial alumina support material has a specific surface area in the range 100 to 300 m²/g.
71. (Withdrawn) A method as claimed in Claim 68, in which the initial alumina support material comprises agglomerated essentially spherical particles having a particle size range whereby at least 80% fall in the range 30 to 120 μ m.
72. (Withdrawn) A method as claimed in Claim 68, in which the initial alumina support material has a pore volume greater than 0.2cm³/g, preferably greater than 0.4cm³/g.
73. (Withdrawn) A method as claimed in Claim 68, in which the impregnated alumina support material is calcined at a temperature in the range 800 to 1200°C.

74. (Withdrawn) A method as claimed in Claim 68, in which the source of a 2-valent metal comprises a source of cobalt, zinc or magnesium.
75. (Withdrawn) A method as claimed in Claim 68, which includes additionally impregnating the alumina support material with a promoter.
76. (Withdrawn) A method as claimed in Claim 75, in which in which the promoter comprises platinum or rhenium.
77. (Withdrawn) A method as claimed in Claim 76, in which the promoter is rhenium and the source of rhenium is selected from perrhenic acid (HReO_4), ammonium perrhenate, rhenium halide(s) and rhenium carbonyl(s).
78. (Withdrawn) A method as claimed in Claim 77, in which the source of the 2-valent metal compound is cobalt nitrate and the rhenium compound is perrhenic acid.
79. (Withdrawn) A method as claimed in Claim 68, which includes additionally impregnating the alumina support material with a stabiliser.
80. (Withdrawn) A method as claimed in Claim 79, in which the stabiliser comprises lanthanum.

81. (Withdrawn) A method as claimed in Claim 68, in which the first impregnation step comprises an incipient wetness treatment in which an aqueous solution of the 2-valent metal compound and optionally a rhenium compound is mixed with the dry support material until the pores are filled, and the impregnated support is then dried, prior to the second calcining step.

82. (Withdrawn) A method as claimed in Claim 68, in which the amount of aqueous solution used in the impregnation is 0.05-2 times larger than the measured pore volume of the catalyst support.

83. (Withdrawn) A method as claimed in Claim 81, in which the drying is carried out at 80 to 120°C.